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ZnO Gas Sensor for Testing Vinegar Acid Concentrations

(Penderia Gas ZnO untuk Menentukan Kepekatan Asid dalam Cuka)

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ABSTRACT

A ZnO gas sensor was successfully prepared by RF sputtering. The maximum sensitivity of the sensor for vinegar test application was at 400°C. The ZnO based sensor showed good sensitivity for vinegar test in the concentration range of 4% to 9%. The work reveals the ability of using ZnO gas sensor to determine the acid concentrations of the vinegars for food requirements.

Keywords: Electrical conductivity; gas sensors; ZnO thin films

ABSTRAK

Penderia gas ZnO telah berjaya dihasilkan dengan percikan RF. Kepekaan maksimum penderia untuk penggunaan dalam pengujian cuka ialah pada 400°C. Penderia berasaskan ZnO menunjukkan kepekaan yang baik untuk pengujian cuka dalam julat kepekatan 4% hingga 9%. Kajian ini menunjukkan keupayaan penderia gas ZnO untuk menentukan kepekatan asid cuka bagi keperluan dalam makanan.

Kata kunci: Kekonduksian elektrik; penderia gas; film nipis ZnO

INTRODUCTION

ZnO is a well known wide band gap semiconductor. It has been studied extensively as the main material for many modern applications such a transparent conductive layer in TFT and solar cell applications and as a light emitting diode (LED) mainly in the UV and blue regions (Morkoç & Ozgur 2009). Many works showed the ability of ZnO as a gas sensor such as ethanol, hydrogen, chlorine and nitrous oxide (Jagadish & Pearton 2006).

Semiconductor gas sensors have been used in food industries for different purposes; they were used to control the quality of meat freshness, orange juice quality and for vinegar classification (Funazaki et al. 1995; Steine et al. 2001; Xiaobo et al. 2003).

Vinegar is commonly used in food preparation and in many industrial and medical applications (Johnston & Gaas 2006). Vinegar can be produced either through the natural process by fermentation of rice, dates, apple seed and sugar, or artificially by diluting the glacial acetic acid to low concentration in the range 5 – 8%. Higher concentrations of acetic acid (up to 15%) may also be used in food processing. Several procedures were employed for the determination of the acid concentrations of vinegar such as capillary electrophoresis, ion-exclusion chromatography, conductimetric detection, attenuated total reflectance of the infrared and acid-base titration (Castro et al. 2002; Lenghor et al. 2002; Moros et al. 2008).

In this work, we report the use of ZnO gas sensor as a tool to determine the acidity concentration of vinegars. This method is cheaper and reliable than the other methods and can be used in vinegar processing.

MATERIAL AND METHODS

n-type silicon wafer of (100) orientation coated with a silicon dioxide layer was used as substrate. Platinum as heating element and two parallel electrodes was patterned and sputtered using A500 Edwards RF dual magnetron sputtering. The distance between the Pt electrodes was about 0.7 mm. High purity zinc metal target was used to produce ZnO film sensor with a thickness of 250 nm and total area of 2×2 mm² by RF reactive sputtering with power of 230 W at sputtering pressure of 2×10⁻² mbar. High-purity argon with 80% oxygen (O₂) was used to produce the plasma. The films were then heat treated at 500°C for 6 h. The sensing measurement of the prepared ZnO gas sensor was explained as in our previous work (Al-Hardan et al. 2009).

The gas response was recorded in a flow-through system using air as a carrier gas at a controlled rate. A bubbler was used to vaporize the liquid acetic acid with different concentrations (Kim et al. 2007). Acetic acid glacial (supplied by J.T. Baker company) was used to prepare the standard solutions in the range 4% to 8% volume concentration, by diluting the acid in deionized water. The vinegar samples were purchased from the Malaysian local markets.

The prepared ZnO films were investigated using a high-resolution PANalytical X-ray diffractometer (HRXRD) for phase identifications and the surface morphology was determined using a field emission scanning electron microscopy (FESEM).

RESULTS AND DISCUSSION

ZnO thin films for gas sensing application were prepared by reactive RF sputtering of high-purity Zn metal target. The produced thickness was about (250 ± 30) nm, as measured by the calibrated quartz crystal monitor. The XRD diffraction pattern (Figure 1) showed that the prepared ZnO on thermally oxidized Si substrate was highly oriented along the *c*-axis, giving a peak at Bragg angle equal to 34.20° , which belongs to the (002) peak of wurtzite structure with reference to JCPDS No. 36-1451. Figure 2 shows the FESEM image of the ZnO film on a thermally oxidized Si which shows a uniform distribution of nanostructure grains of about 20 nm diameter.

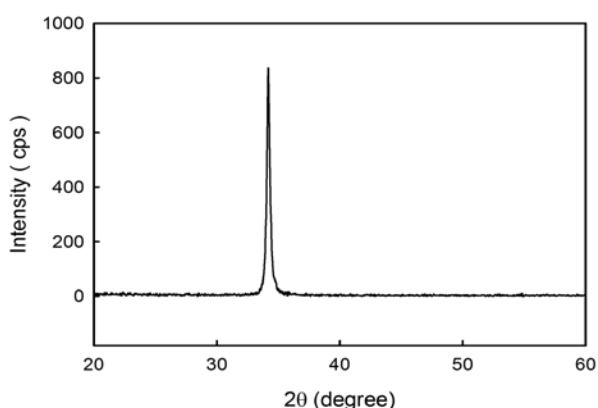


FIGURE 1. The XRD pattern of the ZnO film

The response $S(\%)$ of the sensor for a given concentration of a gas is defined as:

$$S(\%) = \left(\frac{Ra - Rg}{Ra} \right) \times 100,$$

where Rg and Ra is the resistance of the sensor in the acid vapour and in pure air. The sensor showed maximum response at a temperature of 400°C which is the optimum operating temperature. Figure 3 shows the electric resistance of the ZnO gas sensor at different acetic acid concentrations. It clearly showed that the sensor resistance is decreased as the acid concentration is increased.

This proves the *n*-type semiconductor behavior of the ZnO sensor. The repeatability of the sensor behavior is also shown in Figure 4 that showed the same resistance at different time of measurement for fixed acid concentrations.

The calibration curve of the ZnO gas sensor (Figure 5) depicts the linear behavior of the sensor response at the measured range of the acid concentrations. Two commercial vinegar samples from the local market were tested for the acid concentrations; artificial vinegar and the natural vinegar prepared from fermentation of rice. Figure 6 depicts the resistance drop of both vinegar samples. Using the calibration curve, the acid concentration of the artificial vinegar was around 6.4%, while the natural vinegar showed higher acid concentration of 9%. Both showed acceptable acid concentration for food requirements.

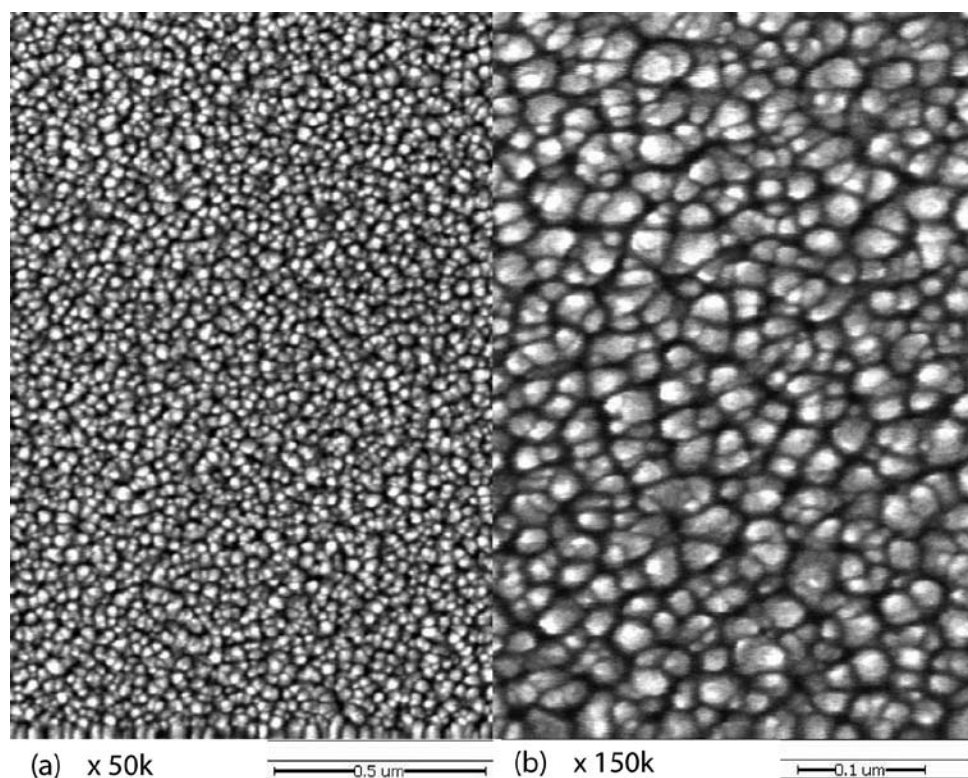


FIGURE 2. FE-SEM image of the RF reactive sputtered ZnO thin films showing nanostructure grain at magnification (a) $\times 50k$, (b) $\times 150k$. The bar length is 0.5 and 0.1 μm , respectively

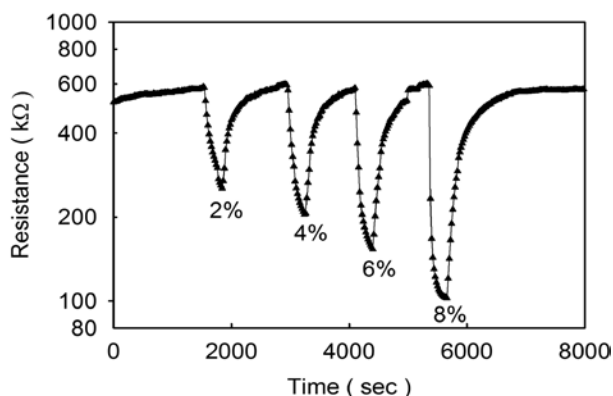


FIGURE 3. Electrical resistance of ZnO gas sensor as a function of the acid

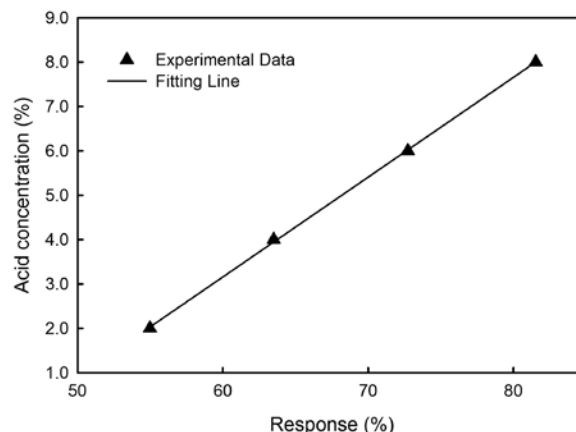


FIGURE 5. Calibration curve of the ZnO sensor

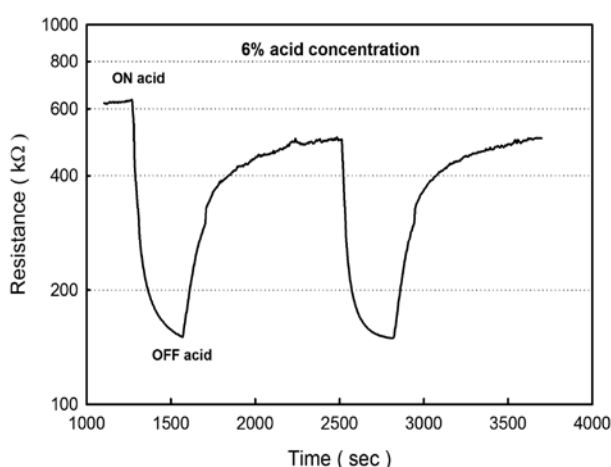


FIGURE 4. Repeatability of ZnO gas sensor behavior at 6% acid

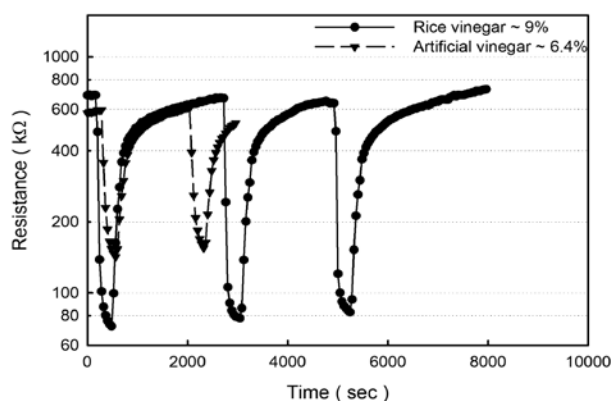


FIGURE 6. Performance of ZnO sensor with tested commercial vinegar

It is well known that metal oxides gas sensors absorbed oxygen from the surrounding atmosphere. At high operating temperatures of the sensor, these oxygen molecules converted to ions by capturing a single or double electron (converting the oxygen molecules to a single or double ion). In the presence of vinegar, the reaction of the acid with the oxygen ions will result in liberation of the electrons back to the conduction band and as a consequence, the carrier concentration will be increased and the resistivity of the sensor decreased (Hellegouarc'h et al. 2001).

CONCLUSION

ZnO gas sensor was used for vinegar concentration measurements. The sensor's output shows a highly dependence on the vinegar concentrations, as well as good repeatability, which makes it a good candidate in quality control applications for the vinegar preparation process.

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REFERENCES

- Al-Hardan, N., Abdullah M.J. & Aziz A.A. 2009. The gas response enhancement from ZnO film for H₂ gas detection. *Applied Surface Science* 255: 7794-7797.
- Castro, R., Moreno M., Natera R., García-Rowe F., Hernández M. & Barroso C. 2002. Comparative analysis of the organic acid content of vinegar by capillary electrophoresis and ion-exclusion chromatography with conductimetric detection. *Chromatographia* 56: 57-61.
- Funazaki, N., Hemmi A., Ito S., Asano Y., Yano Y., Miura N. & Yamazoe N. 1995. Application of semiconductor gas sensor to quality control of meat freshness in food industry. *Sensors and Actuators B: Chemical* 25: 797-800.
- Hellegouarc'h, F., Arefi-Khonsari F., Planade R. & Amouroux J. 2001. PECVD prepared SnO₂ thin films for ethanol sensors. *Sensors and Actuators B: Chemical* 73: 27-34.
- Jagadish, C. & Pearton S. (Eds). 2006. Zinc oxide bulk, thin films and nanostructures. *Processing, Properties, and Applications*, London: Elsevier.
- Johnston, C.S. & Gaas C.A. 2006. Vinegar: Medicinal uses and antiglycemic effect. *MedGenMed*. 8: 61.

- Kim, Y.S., Ha S.-C., Yang H. & Kim Y.T. 2007. Gas sensor measurement system capable of sampling volatile organic compounds (VOCs) in wide concentration range. *Sensors and Actuators B: Chemical* 122: 211-218.
- Lenghor, N., Jakmunee J., Vilen M., Sara R., Christian G.D. & Grudpan K. 2002. Sequential injection redox or acid-base titration for determination of ascorbic acid or acetic acid. *Talanta* 58: 1139-1144.
- Morkoç, H. & Ozgur U. 2009. Zinc oxide. *Fundamentals, Materials and Device Technology*. Weinheim: Wiley-VCH.
- Moros, J., Iñón F. A., Garrigues S. & de la Guardia M. 2008. Determination of vinegar acidity by attenuated total reflectance infrared measurements through the use of second-order absorbance-pH matrices and parallel factor analysis. *Talanta* 74: 632-641.
- Steine, C., Beaucousin F., Siv C. & Peiffer G. 2001. Potential of semiconductor sensor arrays for the origin authentication of pure valencia orange juices. *Journal of Agricultural and Food Chemistry* 49: 3151-3160.
- Xiaobo, Z., Jiewen Z., Shouyi W. & Xingyi H. 2003. Vinegar classification based on feature extraction and selection from tin oxide gas sensor array data. *Sensors* 3: 101-109.

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